Preprint
UCRL-JC-142919

Recent Progress in the Scale-Up of TATB by the VNS Method

R. D. Schmidt, A. R. Mitchell, G. S. Lee, W. T. Quinlin, M. Cates, M. D. Coburn

This article was submitted to
2001 Insensitive Munitions and Energetic Materials Conference,
Bordeaux, France, October 8-11, 2001

August 23, 2001

U.S. Department of Energy

Lawrence
Livermore
National
Laboratory

This work was performed under the auspices of the United States Department of Energy by the University of California, Lawrence Livermore National Laboratory under contract No. W-7405-Eng-48.

Recent Progress in the Scale-Up of TATB by the VNS Method*

Robert D. Schmidt, Alexander R. Mitchell and Gregory S. Lee
Lawrence Livermore National Laboratory, Energetic Materials Center, Livermore, California 94551, USA.

W. Timothy Quinlin and Monty Cates
BWX Technologies, Pantex Plant, Amarillo, Texas, USA

Michael D. Coburn
Los Alamos, New Mexico, USA

EMC
Energetic Materials Center

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Introduction

The explosive TATB is used in the Department of Energy's main charges and boosters, where its extraordinary insensitivity to impact, spark and heat make it highly advantageous. This IHE is also used in booster applications in naval weapons, and is being tested as a main charge fill for hard target penetrator projectiles. (Slides 2-5) In order to meet demand, a continuing supply of TATB will be required. However, no production base exists in the U.S. for TATB production, and processes once used to make TATB are relatively expensive, complicated, and considered environmentally hazardous (Slide 6).

The primary objective of this project is to reestablish the industrial base for TATB production, using LLNL's new Vicarious Nucleophilic Substitution (VNS) methodology. A secondary objective is to enable a reduction in the cost of TATB production, thus making this explosive attractive to U.S. Department of Defense and commercial customers. This presentation will update information presented at the 1998 NDIA IM & EM meeting held in San Diego, California.

TATB Scale-Up

The VNS TATB project made several key advances toward large-scale TATB production. First, after several variations on the VNS approach were thoroughly researched at LLNL (slides 7 & 8), the decision was made to use the commercially available 4-amino-1,2,4-triazole (ATA) as the best reagent to achieve the VNS transformation of picramide to TATB. ATA was found to produce the cleanest TATB in an efficient manner, with excellent yields of product, and without the toxicity and noxious byproducts of earlier VNS reagents. Also, since it contains no chlorine atoms, ATA eliminates the possibility of chloride contamination in the final TATB product, which was a major problem under the original synthesis method (Slide 9).

This synthesis of TATB was then tested at increasingly larger scales—from 1-gram up to 100-gram batches—in the LLNL High Explosive Applications Facility (HEAF) laboratories. Several experiments at each scale were conducted in order to optimize the reaction with respect to reagent concentration, solvent type and purity, and reaction temperature and time, before proceeding to pilot plant-scale work (Slide 10). The optimized synthesis was then tested at the 1-kilogram scale, in a 50 Liter glass reactor at LLNL's Site 300 Chemical Process Area. Several experiments of this scale were conducted, and it was thus demonstrated that further scale-up was feasible (Slide 11).

Having successfully completed the 1-kilogram scale tests, the next step was to transfer the process to the chemical pilot production facility at the DOE Pantex Plant in Amarillo, Texas, for further scale-up and process development. Pantex has been a partner with LLNL on the VNS TATB production project since its inception, because they have the chemical engineering expertise and specialized facilities necessary for production-level explosives work. This turnover process took several months, during which time the Pantex personnel were familiarized with the procedures and results of LLNL's experiments. With this information in hand, Pantex chemical engineers were able to design experiments that would give them information on physical plant requirements and conditions necessary to conduct the VNS synthesis of TATB in their larger Pfaudler reactors.

Before proceeding to these large reactors, Pantex first needed to gather data on how well the process would work under markedly different conditions from those in the laboratory. To accomplish this, they conducted several test reactions in a custom-made, all-glass demonstration reactor. (See Figure 3.) This reactor is shaped like a Pfaudler reactor, but since it is made of glass, it allows the operators to visually verify that chemical mixing and processing are proceeding satisfactorily before using the actual Pfaudler reactor.

Thus far, Pantex chemical engineers have demonstrated that high-purity TATB can be produced in such a reactor, but that some modifications to the laboratory process must be made. Such modifications include changes to chemical addition methods and reaction temperature control, which make the process practical at higher production scales. Additional demonstrations need to be conducted at this scale before the VNS TATB process is attempted in the 30 gallon Pfaudler reactor. (Slide 12)

Product Analysis and Characterization

A critical requirement for weaponization of TATB is that it must be free of certain impurities that could react adversely with materials in other weapons components. While most chemicals can be analyzed for impurities fairly easily, TATB is difficult to analyze primarily because of its extremely low solubility in most solvents. Thus, the team chemists had to modify existing methods to achieve the required analytical sensitivity. (Slides 13-15).

The first method analyzes TATB powder, using Fourier-transform infrared spectroscopy (FTIR). This technique can detect certain impurities down to about 1%. FTIR is especially useful as a quick-screening technique to check whether the VNS reaction has proceeded to completion, or whether additional reaction time is needed. A second method, which can detect other impurities down to 0.5% or less, is direct insertion probe mass spectrometry (DIP-MS). In this method, a very small sample of TATB is inserted directly into a mass spectrometer and the sample is heated under high vacuum, causing it to sublime into the mass detector. Since TATB has a distinctive mass "signature", any other masses that are detected indicate an impurity, which can usually be identified and quantified. A third and very sensitive technique is high pressure liquid chromatography (HPLC), which not only can detect certain impurities, but can be used to "assay" the TATB for total purity. Thus, even though certain impurities might not be directly detectable, the presence of such impurities can be deduced and the percent purity of TATB determined. A fourth and very sensitive method to check TATB purity is differential scanning calorimetry (DSC). The presence of even small amounts of impurities, or even structural irregularities in the TATB crystal, can produce large differences in the DSC output. Although this method cannot identify the nature of the impurities, it is extremely valuable as an overall quality check.

The ultimate goal of these analytical studies is to develop a standard analytical protocol, which can be applied to TATB made not only by the VNS process, but by any process. This way, TATB from any source could be certified to DOE.

In addition to these analytical studies, other types of experiments have been conducted to support the VNS TATB scale-up. One of these is to optimize production of the key starting materials—picramide and ATA. Pantex has done extensive work modifying and scaling the production of picramide by the traditional method, which involves the nitration of commercially available nitroaniline. Using this approach, they have produced many kilograms of picramide for further conversion to TATB. During this work, it was found that picramide can contain small amounts of impurities that result in discoloration of the product TATB. By ensuring that the picramide is free of such impurities, the desired bright yellow-colored TATB results. (Slide 16). With regard to ATA, project chemists have shown that this material can be produced easily and inexpensively from readily available chemicals, thus reducing the cost of acquiring the reagent (which is currently commercially expensive, although artificially so) and eliminating market dependence.

In related studies, LLNL chemists have developed a proprietary method for conversion of other materials to picramide. For example, military stockpiles of the outdated Explosive D can be chemically converted into picramide, thus avoiding the need for nitration and eliminating hazardous acidic waste byproducts. This process is currently being patented. (Slide 17).

Also being studied are alternative solvents and quenching agents for use in the VNS reaction. The current solvent—DMSO—is relatively benign, but has some problems with recyclability and cost. Cheaper recyclable solvents have been investigated, and some improvements to the VNS process may result. Also, it may be possible to quench the VNS reaction with cheaper and more easily handled reagents such as acetic acid or carbon dioxide, while still achieving the requisite purity and particle size of the TATB. Numerous experiments have been conducted in this area, with encouraging results.

Future Project Plans

The next step in this project is to demonstrate the VNS TATB synthesis at the multi-kilogram scale in the Pantex 30 gallon Pfaudler reactor. Once optimized at this scale, it will t be run in the Pantex 100 gallon Pfaudler reactor, and then in larger reactors in the new explosives production facility at Pantex. (Slides 18-20). During each of these stages, optimization of product purity, solvent systems and particle size will be important, so supporting work in these areas will continue at LLNL and Pantex.

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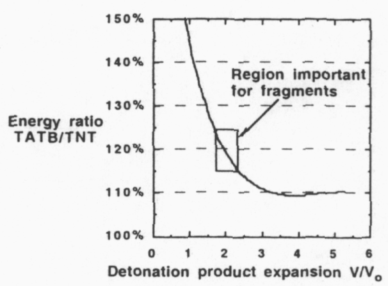
Slide 1

TATB Fact Sheet



Data

Impact sensitivity:	off scale
Shock sensitivity:	≥7.0 GPa
General sensitivity:	extremely low
Failure diameter:	≈10-12 mm
Exotherm (10°C/min):	350°C
Composition:	$C_6H_6N_6O_6$
Density:	1.938 g/cc
Crystal:	triclinic (P1)
Appearance:	yellow
Melting point:	decomposes
Solubility:	generally ins.
ΔH_f:	-154.2 kJ/mol
CTE:	54μm/m-K
λ at 311 K:	0.526 W/m-K

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Slide 2

Applications of TATB

- **Defense**
  - » PBXN-7 Booster Replacement (under Mantech program)
  - » DOE Insensitive Main Charges and Boosters
  - » Insensitive Explosive Fill for Hard Target Penetrator Weapons (under design)
  - » Heat-Stable Gun Propellant Ingredient
- **Commercial**
  - » Thermally Stable Mining Explosives
  - » Nonlinear Optical Materials

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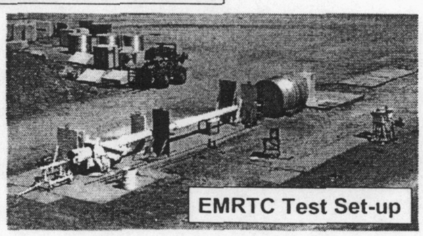
Slide 3

Initial HE Survivability Experiment "Swift Test"


SNL Penetrator


LLNL LX-17 Payload

- » Collaboration between NSWCDD, SNL, LLNL, & NMT
- » Impact conditions
  - 1000 m/s impact velocity
  - 0° obliquity
  - Short standoff to minimize AoA


EMRTC Test Set-up

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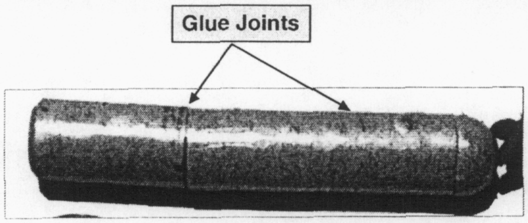
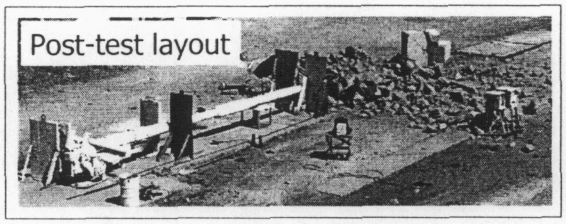
Slide 4

The Results . . .



- No reaction of main charge, all explosive recovered
- Charge conformed to case
- Broken at aft glue joint between HE billets



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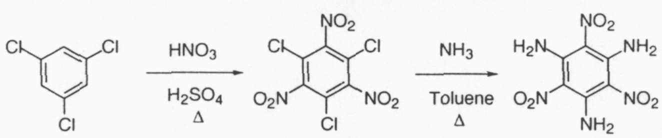
Slide 5

The "Conventional" Route to TATB has Significant Disadvantages



TCB TATB

- Expensive starting material (TCB), and high temperature & pressure process, result in high cost for TATB (currently approx. $US 300-400/kg)
- TCB and reaction by-products are environmental hazards (chloroaromatics) and increase waste disposal costs
- Limited supply of TCB
- Product contamination with NH_4Cl (which can cause weapons material compatibility problems.)
- No current U.S. supplier (U.S. national security concern).

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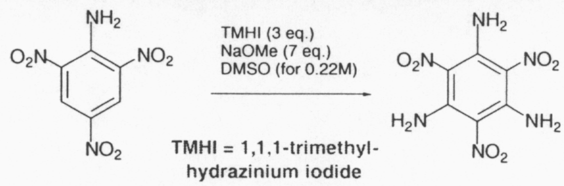
Slide 6

First Advance Toward a New TATB Synthesis: VNS Amination with TMHI



Picramide **TATB**

Advantages of this approach:

- conducted at room temperature, complete in 3 hours
- yields high quality (> 99%) TATB in 80-90% yield
- avoids use of chlorinated aromatic precursors

However, practical problems during scale-up (↓ purity & yield; noxious gas handling) led us to check other VNS routes.

Reference: Mitchell, A. R., Pagoria, P. F. and Schmidt, R. D., US Patent 5,569,783 (October 29, 1996)

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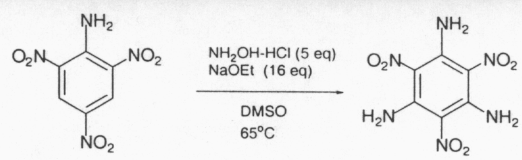
Slide 7

Conversion of Picramide to TATB using Hydroxylamine



Picramide **TATB**

<u>This approach is probably the cheapest way to make TATB.</u>

However, in our experiments, it typically produced only moderate yields of 97% pure TATB, with varying degrees of green discoloration (believed to be due to nitroso-analogues of TATB.)

Work by Aerojet Corp. has discovered improvements to this route leading to higher quality and yield of TATB. (Details *proprietary*)

Reference: Mitchell, A. R., Pagoria, P. F. and Schmidt, R. D., US Patent 5,633,406 (May 27, 1997)

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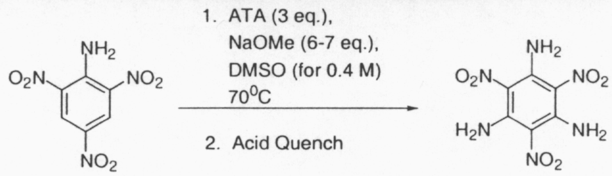
Slide 8

We Achieved the Best Results Using Aminotriazole (ATA) as the VNS Reagent



ATA = 4-amino-1,2,4-triazole

85-95% yield

Advantages of this approach:

- High yield, high purity (99+% pure TATB)
- Higher concentrations allowed (reduces solvent & waste)
- Improved product appearance (clean, yellow product)
- No possibility of halide contamination in TATB

Reference: Mitchell, A. R., Pagoria, P. F. and Schmidt, R. D., US Patent 5,633,406 (May 27, 1997)

Slide 9

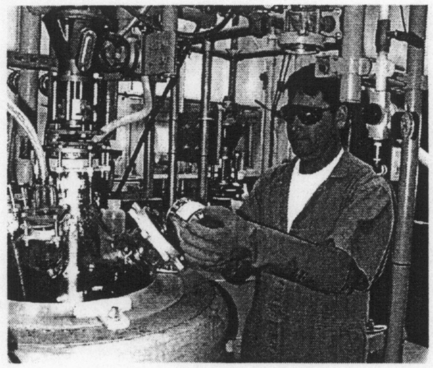
Further Studies Were Conducted to Optimize the Process

- **Optimize Reaction Conditions**
  - » **Maximize solution concentration**
  - » **Minimize amount of reagents needed**
  - » **Determine minimum reagent purity required**
- **Increase Product TATB Particle Size and Purity**
- **Investigate Alternate Solvent Systems**
- **Prove Process at Larger Scale**

Slide 10

Kilogram-Scale Experiments

- Run using ATA reagent
- 50L Glass Reactor at LLNL Site 300
- 80% yield of TATB
- Product purity 99% by FTIR and DIP/MS
- Initial tests showed slight discoloration of product, due to impurity in starting material (resolved)
- 30 micron mean particle size



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Slide 11

Initial Pilot Plant Results at Pantex

- First tests were done in a 10 L glass reactor simulating a Pfaudler reactor.
  - » Allows for visual process checking prior to further scale-up
  - » Simplifying improvements were made to reagent addition methods
- First attempt in larger reactor failed to produce TATB, due to poor quality of NaOMe used.
  - » Surface “passivation” by Na_2CO_3 (see our 1998 NDIA paper)
  - » *NaOMe must be checked prior to use!*
- Subsequent attempts have produced very good quality TATB (99+%) in good yield (75%)
  - » Will optimize at this scale before proceeding

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Slide 12

Test & Analysis of Product TATB

- One of the project goals is to develop standardized methods for TATB quality certification. Among the analytical techniques being used are:

> Fourier Transform Infrared (FTIR) Spectroscopy
> Direct Insertion Probe Mass Spectrometry (DIP/MS)
> High Pressure Liquid Chromatography (HPLC)
> Elemental Analysis (esp. for S, Cl)
> Chemical Reactivity Test (CRT)
> Differential Scanning Calorimetry (DSC)
> Drop Hammer Sensitivity
> Spark & Friction Sensitivity
> Particle Size Distribution Analysis
> Scanning Electron Microscopy

Ref: Schmidt, et. al., Proc. 31st Int. Annual Conf. ICT, 2000, pp. 37.1-37.10; more detail in LLNL report UCRL-VG-136606.

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Slide 13

Small Scale Test Results of TATB (from 1kg ATA Reaction)

Drop Hammer:	>177 cm
Spark Sensitivity:	0/10 @ 1.0 Joules
Friction Sensitivity:	0/10 using 36 kg weight
CRT:	0.009 cc/0.25g
DSC:	367 °C (onset), sharp peak

...i.e., analytically *at least as good as "conventional" TATB!*

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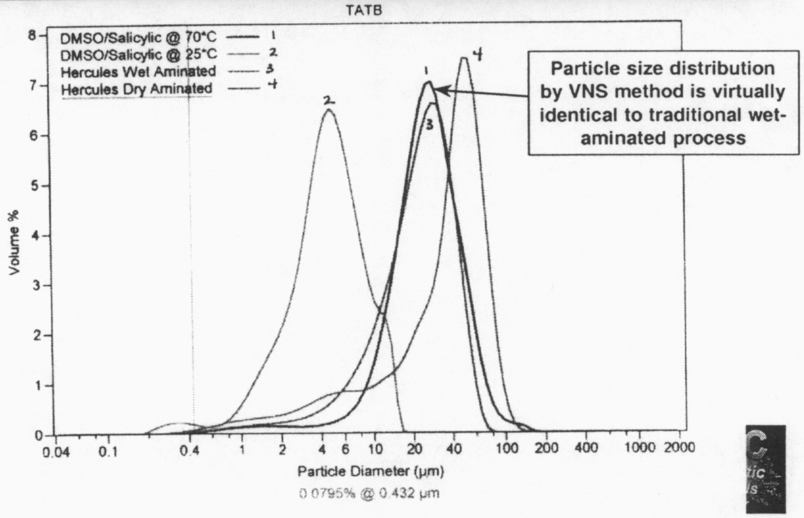
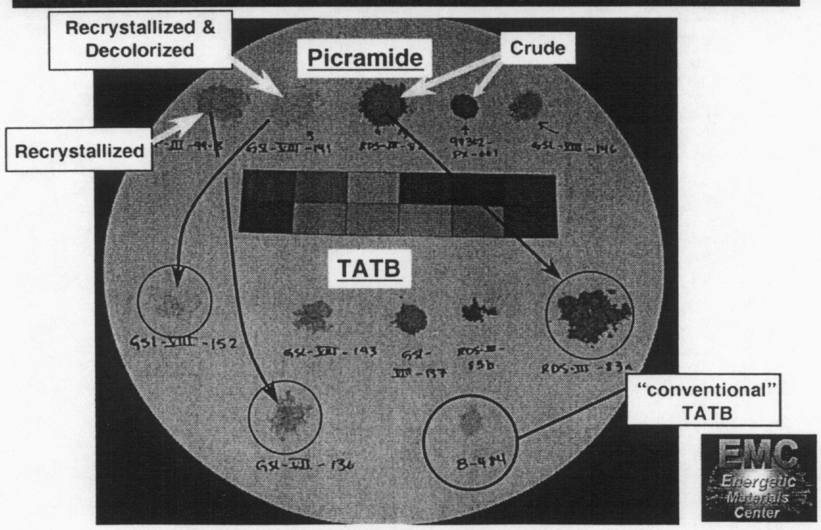
Slide 14

VNS TATB Product Particle Size Distribution (Salicylic Acid Quench)



Slide 15

Color of the Starting Material has Dramatic Effect on TATB Product Color



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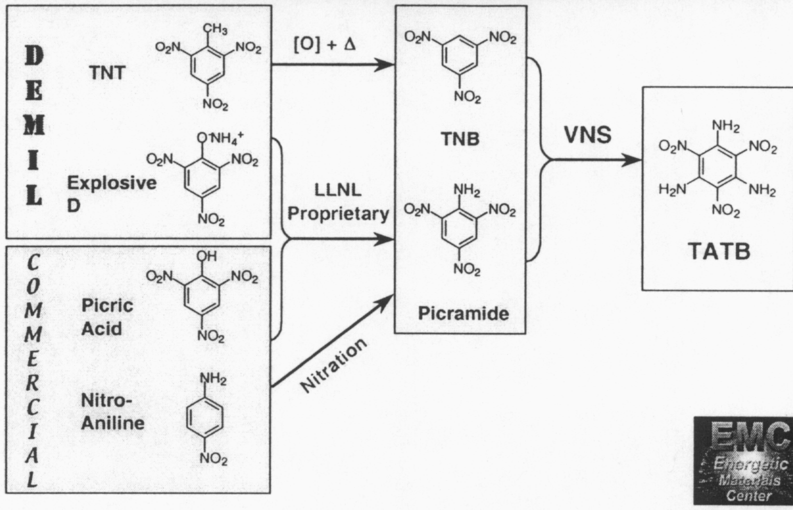
Slide 16

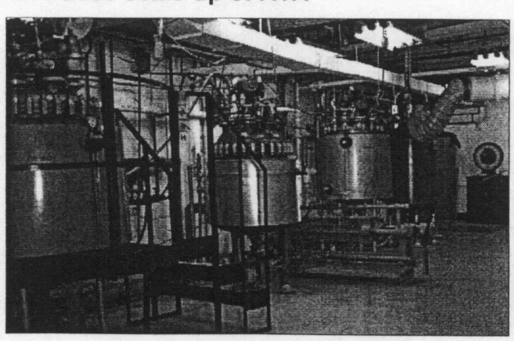
Multiple Feedstocks Could Be Used to Make TATB by the VNS Process



Slide 17

Next Step

- **Pilot Plant scale-up work at Pantex**
  - » 30- and 100-gallon reactors (FY 2002-3)
  - » (15 - 60 kg TATB per batch (current conditions))
  - » In-house scale-up of ATA



Slide 18

Future Work

- **Further Pilot Plant scale-up work at Pantex**
  - » Large scale demonstration (FY 2004) in new production facility (in final construction phase)
- **Process improvements**
  - » Particle size (30-60 μm average desired)
  - » Solvent and waste stream reduction
- **TATB product performance testing.**
  - » Formulation characteristics
  - » Explosive performance
  - » Stability and materials compatibility, etc.
- **License and transfer optimized process for industrial scale production.**

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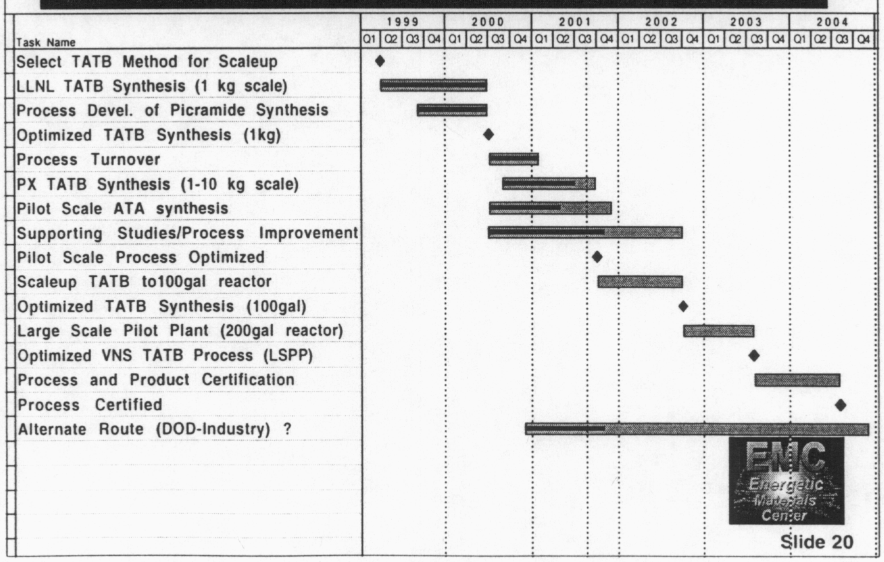
Slide 19

VNS TATB Project Timeline



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Slide 20

Acknowledgements

- Work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract No. W-7405-ENG-48.
- Funding for this work was provided by:
  - » The USDOE Advanced Design and Production Technologies (ADAPT) Process Development Program
  - » James Q. Wheeler (Director, US Army Defense Ammunition Center) and the Joint DOD/DOE Munitions Technology Program, Munitions Life Cycle Technology R&D Program

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Slide 21